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A New Method for Solving the Coupled Equations in the Adiabatic Representation.

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Foreward

In electron transfer reaction between the oxidized
form of A and the reduced form of B,

$$A_{ox} + B_{red} \rightarrow A_{red} + B_{ox} \, ,$$

there is the "diabatic" potential surface formed from the
electronically-uncoupled reactants and environment and the
diabatic surface formed from the electronically-uncoupled
products and environment. The electronic interaction between
A and B introduces new surfaces--the adiabatic potential energy
surfaces, discussed for example by the principal investigator
in Ann. Rev. Phys. Chem., 15, 155 (1964). It is desirable to
develop a numerical method to treat the dynamics of molecular
motion on those surfaces, to calculate the reaction rate. In
the present Technical Report Dr. Babamov formulates such a
method. In practice, to reduce the number of quantum states
needed in the computation one would need to simplify the actual
many-dimensional problem before applying the method. One such
application has been made by Drs. Babamov and DiGiacomo of
this laboratory.

R. A. Marcus
Principal Investigator

A New Method for Solving the

Coupled Equations in the Adiabatic

Representation

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ABSTRACT

A new method for solving the coupled equations in the adiabatic
representation which arise in quantum mechanical treatment of atomic and
molecular collisions is developed. The solutions of the uncoupled
adiabatic equations, obtained from the coupled equations in the adiabatic
representation by neglecting the coupling terms, are used to derive a set
of new exact equations for the purely inelastic effects of the collision.
The solutions of the new equations are practically nonoscillatory and
can be solved numerically with little computational effort.

I. INTRODUCTION

The computational wave mechanical treatment of inelastic atomic and mole-
cular collisions is frequently reduced to solving a set of coupled ordinary
linear differential equations.[1-5] The coupled ordinary differential equations
are obtained by expanding the solution of the time-independent Schrodinger
equation for the system in a product basis set consisting of known wavefunc-
tions for the internal motion and for the angular relative motion, multiplied
by unknown coefficients which depend on the relative radial motion coordinate.

The choice of the basis set functions for the internal motion determines
the structure of the resulting coupled equations. When the wavefunctions for
the internal motion of the separated particles are used in the basis set the
coupled equations are said to be in the diabatic representation. On the
other hand when the solutions of the Schrodinger equation for the colliding
pair at each fixed interparticle distance are used in the expansion, the resulting
equations are in the adiabatic representation.[3-6]

The coupled equations in the diabatic representation are used often
in the treatment of vibrationally and rotationally inelastic molecular
collisions occurring on a single electronic potential energy surface.[7,8]
Developing methods for solving the coupled equations in the diabatic repre-
sentation has thereby received considerable attention, particularly in the
past decade, and a number of highly efficient methods for solving them have
been developed.[7-10]

The equations in the adiabatic representation are frequently
encountered when a rigorous treatment of an electronically nonadiabatic atomic
collision is attempted.[11,12] They have a somewhat more complex mathematical
structure and developing methods for solving them has received relatively
little attention in the literature.[13,14] The most widely used of the new[7-9]

efficient methods for solving the equations in the diabatic representation have not been adapted for solving the adiabatic equations. Although a direct numerical integration of the equations in the adiabatic representation is possible and has been conducted for some model problems[13,14] the only method used has been direct numerical integration of the coupled equations based on a polynomial approximation to the wavefunction. The inelastic atomic collisions have in practice usually been treated instead by solving a set of diabatic equations constructed in some approximate manner,[15] or still more approximately by solving the corresponding so-called classical path equations.[16] The latter equations are obtained by treating the electronic motion quantum mechanically and the relative motion of the atoms classically.

In this paper a stable and efficient method for solving a set of coupled ordinary differential equations in the adiabatic representation is outlined. The method can be used for treating electronic transitions and charge transfer in atomic collisions, which can be rigorously formulated in the adiabatic representation[3,12] The electronic transitions in molecular collisions can also be treated by the present method since they are also conveniently formulated in the adiabatic representation.[13]

Both the spatial extension of the coupling region[17] and the number of coupled states[18] are smaller in the adiabatic representation than in the diabatic one. Since the equations in the diabatic representation and the equations in any other representation in which both diabatic and adiabatic coupling elements appear can be straightforwardly converted into a pure adiabatic representation[3,5] the present method could also be used in cases when a diabatic or some other representation is most convenient for initial formulation of the problem.

The Hamiltonian for the system and the usual quantum mechanical coupled equations are given in Sec. II. The structure and the symmetry properties of the coupled equations are analyzed in the Appendix.

The solution of the coupled equations is performed in three stages. First, a set of uncoupled second order differential equations, obtained from the equations in the adiabatic representation by neglecting the coupling matrix elements, is solved using one of the standard methods in the literature.[8] The solutions of these uncoupled equations are then used in Sec. III to convert the equations in the adiabatic representation into a set of new first-order coupled differential equations by means of a variation of constant type of treatment. The dependent variables in these new equations are typically much more slowly varying than the original ones. The resulting first-order equations (Eq. 3.14) can then be solved using one of the standard methods to evaluate the scattering matrix elements.

The method is illustrated in Sec. IV using as an example the evaluation of inelastic transition probabilities for a $He^+ + Ne$ collision in the two-state approximation. The model problem used has been treated previsouly by other methods, and so the feasibility of the present treatment can be verified.

II. THE COUPLED EQUATIONS

The Schrodinger equation for a system of two colliding particles which have internal structure is given in reduced units by:

$$H\Psi = [-\nabla_R^2 - \Sigma \nabla_r^2 + V(\underset{\sim}{r},\underset{\sim}{R})] \quad \Psi = E\Psi \tag{2.1}$$

where the vector $\underset{\sim}{R}$ is defined by its magnitude R and the two angles describing its orientation denoted collectively by $\underset{\sim}{\Omega}$; R denotes the relative position of the centers of mass of the two particles. The vector $\underset{\sim}{r}$ denotes all internal coordinates. The sum $\Sigma\nabla_r^2$ is over all the internal coordinates.

The solution of the time-independent Schrodinger equation with the Hamiltonian (2.1) can be expanded in a product basis set consisting of a set of known wavefunctions $\chi(\underset{\sim}{r},\underset{\sim}{\Omega};R)$ which depend on $\underset{\sim}{r}$ and $\underset{\sim}{\Omega}$ for every value of R, multiplied by R-dependent coefficients:[12a]

$$\Psi = \sum_i \psi_i(R) \; \chi_i \; (\underset{\sim}{r},\Omega;R) \tag{2.2}$$

It is also convenient to choose χ_i as a set of real functions.

Substituting (2.2) into the Schrodinger equation and integrating over $\underset{\sim}{r}$ and $\underset{\sim}{\Omega}$ a set of coupled ordinary differential equations for the radial coefficient wavefunctions $\psi_i(R)$ is obtained.[3,4,12]

$$p^2\psi_i + \sum_j [2P_{ij}p\psi_j + B_{ij}\psi_j + V_{ij}\psi_j] = E\psi_i \tag{2.3}$$

where

$$p = -i\partial/\partial R, \quad P_{ij} = \langle\chi_i|p|\chi_j\rangle, \quad B_{ij} = \langle\chi_i|p^2|\chi_j\rangle \tag{2.4a}$$

and

$$V_{ij} = V_{ji} = \langle\chi_i|H'|\chi_j\rangle \tag{2.4b}$$

H' contains the entire potential plus the kinetic energy terms for the internal coordinates $\underset{\sim}{r}$ and for the orientational coordinates $\underset{\sim}{\Omega}$. If a rotating coordinate system is used H' also contains all the terms stemming from the rotation of the coordinate system.[12] The brackets $\langle \ \rangle$ denote integration over $\underset{\sim}{r}$ and $\underset{\sim}{\Omega}$

Eq. (2.3) can be written compactly in matrix notation:

$$[\underline{\underline{I}}p^2 + 2\underline{\underline{P}}p + \underline{\underline{B}} + \underline{\underline{V}}]\ \underset{\sim}{\psi} = E\underset{\sim}{\psi} \quad , \tag{2.5}$$

where $\underset{\sim}{\psi}$ is a column vector with elements ψ_i and $\underline{\underline{P}}$, $\underline{\underline{B}}$, and $\underline{\underline{V}}$ are square matrices with elements given by (2.4), while the symbol $\underline{\underline{I}}$ denotes unit matrix.

Applying p to the scalar product of two χ_i's, and noting that $\langle \chi_i | \chi_j \rangle$ equals δ_{ij} one has

$$0 = p\langle \chi_i | \chi_j \rangle = -\langle p\chi_i | \chi_j \rangle + \langle \chi_i | p\chi_j \rangle = -P_{ji}^* + P_{ij} \quad , \tag{2.6}$$

Thus, $\underline{\underline{P}}$ is a hermitian matrix. If the basis set χ_i is complete the matrix $\underline{\underline{B}}$ can be expressed in terms of the matrix $\underline{\underline{P}}$ and its derivative[3]

$$\underline{\underline{B}} = \underline{\underline{P}}^2 + (p\underline{\underline{P}}), \tag{2.7}$$

where the operator p is not considered to act beyond the close of the parentheses, and the elements of $\underline{\underline{P}}^2$ are obtained from those of $\underline{\underline{P}}$ by matrix multiplication. Using (2.7) the coupled equations (2.5) become

$$(\underline{\underline{T}} + \underline{\underline{V}})\ \underset{\sim}{\psi} = E\underset{\sim}{\psi} \tag{2.8}$$

$$\underline{\underline{T}} = \underline{\underline{I}}p^2 + 2\underline{\underline{P}}p + (p\underline{\underline{P}}) + \underline{\underline{P}}^2 = (\underline{\underline{I}}p + \underline{\underline{P}})^2 \tag{2.9}$$

It is in practice easier to evaluate $p\underline{\underline{P}}$ and $\underline{\underline{P}}^2$ in (2.9) than the $\underline{\underline{B}}$ in (2.5) and (2.4) since evaluation of $\underline{\underline{B}}$ requires numerical evaluation of second derivatives of χ_i.

Eq. (2.8) is a set of ordinary differential equations, usually an infinite set, and is a partly integrated form of the Schrodinger equation, fully equivalent to (2.1). The matrix operator on the l.h.s. of (2.8) then represents

the Hamiltonian operator H from (2.1) as applied to the space of coefficient wavefunctions $\dot{\psi}_i(R)$. The matrix operator $\underline{T}$ in (2.9) arises from the radial part of the kinetic energy operator in (2.1) and can be viewed as the radial kinetic energy part of the matrix Hamiltonian operator. The matrix $\underline{V}$ represents an effective matrix potential for the radial motion.

It is convenient for simplifying the following discussion to consider instead of Eq. (2.8), which involves the vector $\underset{\sim}{\psi}$, the following matrix equation:

$$[\underline{I}p^2 + 2\underline{P}p + (p\underline{P}) + \underline{P}^2 + \underline{V}]\underline{\psi} = E\underline{\psi} \tag{2.10}$$

where $\underline{\psi}$ denotes an n by n square matrix which contains as columns n linearly independent vector solutions $\underset{\sim}{\psi}$ of (2.8).

The matrix $\underline{V}$ in (2.10) can be rewritten as

$$\underline{V} = \underline{V}^O + \underline{V}^{int} \; ; \; V^O_{ij} = \delta_{ij} \; (\epsilon_i + \ell_i(\ell_i+1)/R^2) \tag{2.11}$$

where ϵ_i is the eigenvalue of the internal ($\underset{\sim}{r}$-dependent) part of the basis function χ_i, and ℓ_i is the angular momentum associated with the angular ($\underset{\sim}{\Omega}$ dependent) part of the χ_i. In the limit of large R the adiabatic coupling matrix $\underline{P}$ and the potential coupling matrix $\underline{V}^{int}$ vanish and the coupled equations (2.11) can be written as a set of uncoupled equations

$$(\underline{I}p^2 + \underline{V}^O)\underline{\psi} = E\underline{\psi} ; \tag{2.12}$$

the diagonal angular terms $\ell_i(\ell_i+1)/R^2$, which also vanish for large R, have been retained in (2.12) to simplify the structure of the phases in the scattering matrix. The solution of (2.12), which for large R is equivalent to (2.11) is given in terms of Riccati-Bessel functions and can be written for large R using the assymptotic form of the Riccati-Bessel functions as:

$$\underline{\psi}(R) = \underline{F}^+(R)\underline{C}^+ + \underline{F}^-(R)\underline{C}^- . \qquad (R \to \infty) \tag{2.13}$$

where $\underline{\underline{F}}^{\pm}$ are diagonal matrices with elements

$$F_{Ti}^{+}(R) = (1/2k_i)^{1/2} \exp[\pm i(k_i R - \ell_i \pi/2)] \qquad (2.14)$$

i.e. F_{ii}^{+} and F_{ii}^{-} are the diagonal elements of the two linearly-independent asymptotic solutions of (2.14). The factor $(1/2)^{1/2}$ has been inserted to normalize them to a Wronskian, $F_{ii}^{+}\dot{F}_{ii}^{-}-\dot{F}_{ii}^{+}F_{ii}^{-}$, equal to $-i$, where the dot denotes d/dR. The $\underline{\underline{C}}^{\pm}$ in (2.13) are integration constant matrices. The choice of the phases in (2.14) is a matter of convention; different phases will be used in Sec. 3 to define the purely inelastic scattering matrix.

The scattering matrix (S-matrix) is usually introduced as the matrix that converts $\underline{\underline{C}}^{-}$ in (2.13) into $\underline{\underline{C}}^{+}$[1,2].

$$\underline{\underline{C}}^{+} = \underline{\underline{S}}\,\underline{\underline{C}}^{-} \qquad (2.15)$$

The choice of the basis set $X_i(\underline{r},\underline{\Omega})$ in (2.2) determines the structure of the matrices in (2.10). Two particular choices for which the structure of (2.10) is qualitatively simplified are of practical interest. If the basis set is chosen to be the set of eigenfunctions of the internal orientational part of the Hamiltonian for large R the matrix $\underline{\underline{P}}$ vanishes identically (due to the lack of dependence of the basis set on R) and all the coupling in the differential equation is contained in the effective potential energy matrix $\underline{\underline{V}}$. Such basis set is a diabatic basis set and the resulting set of coupled equations is in the diabatic representation.[4]

The coupled equations in the diabatic representation are of the form

$$(\underline{\underline{I}}p^2 + \underline{\underline{V}})\underline{\underline{\psi}} = E\underline{\underline{\psi}} \qquad (2.16)$$

If the basis set is chosen instead to be the set of eigenfunctions of the
internal-orientational part of the Hamiltonian, i.e., of H' at every R, the off-diagonal
elements of $\underline{\underline{V}}$ (2.4b) vanish identically, so that all the coupling is dynamic, and
it is contained in the kinetic energy part of the Hamiltonian. The diagonal
elements of $\underline{\underline{V}}$ then obey the well known non-crossing rule,[19] i.e., they cannot
cross at any R unless the matrix element of $\underline{\underline{P}}$ that couples them vanishes.

In the adiabatic representation, the equations are of form:

$$[\underline{\underline{I}}p^2 + 2\underline{\underline{P}}p + (p\underline{\underline{P}}) + \underline{\underline{P}}^2 + \underline{\underline{V}}]\underline{\psi} = E\underline{\psi} \tag{2.17}$$

where $\underline{\underline{V}}$ is a diagonal matrix with elements.

$$V_{ij} = \delta_{ij}\epsilon_i, \tag{2.18}$$

and ϵ_i is the i-th eigenvalue of H' for a given R. All the coupling is contained
in the kinetic energy matrix, which in turn is given in terms of the adiabatic
coupling matrix $\underline{\underline{P}}$.

It should be noted that in some cases (e.g., when the angular coupling is
not negligible) the eigenfunctions of the internal-orientational part of the
Hamiltonian H' for every R may be difficult to evaluate directly. In such
cases using an approximation to the adiabatic basis set (e.g., product of
eigenfunctions of the internal part of H multiplied by spherical harmonics)
would lead to nonzero of-diagonal elements in $\underline{\underline{V}}$ and the coupled equations (2.10)
will not be in the adiabatic representation. The coupled equations can then
be converted to the adiabatic representation by diagonalizing the potential
energy matrix $\underline{\underline{V}}$ at every R, and transforming the kinetic energy matrix
accordingly. The same can be done when the diabatic representation can be
formulated and it is easier to set up. The transformation matrices needed
to convert the equations between the adiabatic, diabatic and any other general

representation are given in the appendix. A rigorous discussion of the symmetry properties of the coupled equations is also given in the appendix.

Once a set of equations in the adiabatic representation has been constructed, either directly or by transforming the equations in some other representation the method described in the next section can be used to construct their solution.

III. EQUATIONS FOR THE AMPLITUDE COEFFICIENTS

Using Eq. (2.9), Eq. (2.10) can be rewritten as

$$(\underline{\underline{I}}p + \underline{\underline{P}})^2 \, \underline{\psi} = \underline{\underline{\pi}}^2 \underline{\psi} \qquad , \; \pi_{ij} = (E-V_{ij})\delta_{ij}. \tag{3.1}$$

For most atomic collisions the elements of the coupling radial momentum
matrix $\underline{\underline{P}}$ in (2.10) are small throughout the collision range.   In such
cases a good approximation to the solution of (3.1)   can be obtained
by neglecting the coupling matrix $\underline{\underline{P}}$ and solving the resulting set of uncoupled
second order differential equations.

$$\underline{\underline{I}}p^2\underline{\phi} = \underline{\underline{\pi}}^2\underline{\phi} \tag{3.2}$$

Equation (3.2) can be solved numerically more easily than (3.1);
some good analytic approximations also exist.[20]   Approximating the solu-
tion of (3.1) by a solution of (3.2) is for a system of two atoms essentially,
the Born-Oppenheimer approximation.[11] It corresponds physically to the neglect
of the effect of the relative atomic motion on the electronic states of the
system.   For slow atomic collisions the Born-Oppenheimer approximation is
usually already a very good one except for one important special case: If
two or more matrix elements of the diagonal matrix $\underline{\underline{V}}$ are nearly degenerate
for some values of the radial coordinate R the corresponding matrix elements
in the matrix $\underline{\underline{P}}$ become often large in the same region and cannot be neglected
any more. The occurrence of such avoided crossing of the diagonal matrix
elements of the matrix $\underline{\underline{V}}$ as a function of the radial coordinate is the main
reason for electronic transitions in slow atomic collisions. The breakdown of
the Born-Oppenheimer approximation in this case is localized to a relatively
narrow spatial region around the avoided crossing; Eg. (3.2) is however,
still an excellent approximation to (3.1) outside the avoided crossing region.

The solution of (3.1) subject to a given initial condition at small R can be factored at any point into the solution of (3.2) subject to the same initial condition and a set of additional correction factors which reflect the nonvanishing of the matrix $\underline{\underline{P}}$.

The main features and the typical oscillatory structure of the solution of (3.1) are already contained in the solution of (3.2). The additional correction factors vary more slowly with R than the solution of (3.1) itself and are practically constant outside the region where the matrix $\underline{\underline{P}}$ is large. In the remainder of this section the differential equations for the above correction factors are derived.

Any solution of each of the uncoupled equations

$$p^2 \phi_{ii} = \pi^2_{ii} \phi_{ii} \tag{3.3}$$

can be written as a linear combination of two linearly-independent solutions of (3.3) denoted by U^+_{ii} and U^-_{ii},

$$\phi_{ii} = U^+_{ii} C^+_{ii} + U^-_{ii} C^-_{ii} . \tag{3.4}$$

The two linearly independent solutions of (3.3), U^+_{ii} and U^-_{ii}, will be taken to be the solutions with the asymptotic form

$$U^\pm_{ii} \sim [1/(2k_i)^{1/2}] \exp \left[\pm i(k_i R - \varsigma_i) \right] . \tag{3.5}$$

which are complex conjugates of each other *and* have been normalized in such a way that their Wronskian, $U^+_{ii} \dot{U}^-_{ii} - \dot{U}^+_{ii} U^-_{ii}$, is equal to $-i$.

The general solution of (3.2) can then be written in form of a linear combination of the two solutions $\underline{\underline{U}}^+$ and $\underline{\underline{U}}^-$.

$$\underline{\phi} = \underline{\underline{U}}^+ \underline{C}^+ + \underline{\underline{U}}^- \underline{C}^- . \tag{3.6}$$

The only nonvanishing elements of the matrices $\underline{\underline{U}}^+$ are the diagonal ones defined by (3.5), while the $\underline{\underline{C}}^\pm$ are diagonal constant matrices.

One seeks now a solution to the coupled adiabatic equations (3.1) in terms of the solutions of (3.2) $\underline{\underline{U}}^+$ and $\underline{\underline{U}}^-$,

$$\underline{\psi} = \underline{\underline{U}}^+\underline{\alpha}^+(R) + \underline{\underline{U}}^-\underline{\alpha}^-(R) \qquad (3.7)$$

with the coefficients $\alpha_{ij}^\pm$ being functions of R. Since the matrices $\underline{\underline{U}}^\pm$ are diagonal, the elements of $\underline{\psi}$ are given by

$$\psi_{ij} = U_{ii}^+\alpha_{ij}^+(R) + U_{ii}^-\alpha_{ij}^-(R). \qquad (3.8)$$

Since there are twice as many $\alpha_{ij}^\pm$ in (3.7) as there are wave functions ψ_{ij} from which the $\alpha_{ij}^\pm$ can be determined, one is free to impose n^2 constraints in form of n^2 algebraic or differential relations between the $\alpha_{ij}^\pm$, where n is the size of the matrices in (3.1). While the n^2 constraints are completely arbitrary at this point, the choice of the constraint will affect the ease with which the resulting equations will be solved. The most slowly changing coefficients α_{ij}^+ result from a constraint that makes the α_{ij}^+ come closest to being an average of the absolute value of the rapidly oscillating wavefunction solutions of the coupled equations. In the classical limit, when the period of oscillations of the wavefunctions goes to zero the $\alpha_{ij}^\pm$ become a measure of the probability of finding the particle in the channel i, for a system initially in channel j, since if one integrates the absolute square of the wavefunction in a small region the value will be proportional to the value of the absolute value square of the much smoother functions α_{ij}^+.

Comparing (3.1) and (3.2) it can be seen that applying the operator $\underline{\underline{F}} = (\underline{\underline{I}}p+\underline{\underline{P}})$ twice to the solution of (3.1) has the same effect as applying the operator p twice to the solutions of (3.2). The operator $\underline{\underline{F}}^2$,

$$\underline{\underline{F}}^2 = (\underline{\underline{I}}p + \underline{\underline{P}})^2 , \tag{3.9}$$

when applied on the solutions of (3.2) thus acts effectively only on the elastic part of the solution, given by the solutions of (3.3), $\underline{U}^{\pm}$, but not on the additional factors, $\underline{\alpha}^{\pm}$.

$$\underline{\underline{F}}^2 \underline{U}^+ \underline{\alpha}^+ + \underline{U}^- \underline{\alpha}^- = (p^2 \underline{U}^+)\underline{\alpha}^+ + (p^2 \underline{U}^-)\underline{\alpha}^- \tag{3.10}$$

Defining the operator $\underline{\underline{F}} = (\underline{\underline{I}}p + \underline{\underline{P}})$ itself in an analogous way would then yield the equations for separating the elastic and inelastic effects as first order differential equations. The operator $\underline{\underline{F}}$ with such properties, which can be called an adiabatic momentum operator, can be formally defined by

$$\underline{\underline{F}}^n \underline{U} = p^n \underline{U} \qquad n=1, 2$$

$$\tag{3.11}$$

$$\underline{\underline{F}}(p^n \underline{\underline{\alpha}}^{\pm}) = 0. \qquad n=0, 1$$

Applying this $\underline{\underline{F}}$ twice to $\underline{\psi}$, yields the same result as applying the $\underline{\underline{F}}^2$ given by (3.9). From (3.11) one finds

$$\underline{U}^+ p\underline{\underline{\alpha}}^+ + \underline{U}^- p\underline{\underline{\alpha}}^- + \underline{\underline{P}}(\underline{U}^+ \underline{\alpha}^+ + \underline{U}^- \underline{\alpha}^-) = 0 \tag{3.12}$$

The above constraint is clearly not the usual variation of constant constraint [21-23] (namely that $\underline{U}^+ p \underline{\alpha}^+ + \underline{U}^- p \underline{\alpha}^-$ equals zero).

Using (3.12) and (3.2), Eq. (3.1) can be reduced to a set of first order differential equations for the $\underline{\alpha}^{\pm}$.

$$\frac{d}{dR}\begin{bmatrix}\underline{\underline{\alpha}}^{+}\\[6pt]\underline{\underline{\alpha}}^{-}\end{bmatrix}=\begin{bmatrix}\underline{\underline{U}}^{-} & -\underline{\underline{U}}^{-}\\[6pt]-\underline{\underline{\dot{U}}}^{+} & \underline{\underline{\dot{U}}}^{+}\end{bmatrix}\begin{bmatrix}\underline{\underline{P}} & 0\\[6pt]0 & \underline{\underline{P}}\end{bmatrix}\begin{bmatrix}\underline{\underline{U}}^{+} & \underline{\underline{U}}^{-}\\[6pt]\underline{\underline{\dot{U}}}^{+} & \underline{\underline{\dot{U}}}^{-}\end{bmatrix}\begin{bmatrix}\underline{\underline{\alpha}}^{+}\\[6pt]\underline{\underline{\alpha}}^{-}\end{bmatrix}\qquad(3.13)$$

Since the coupled equations (3.13) have real coefficients a purely real set of solutions can be constructed. Since a solution post-multiplied by a constant matrix is also a solution of (3.13) the two real matrix solutions can be used to generate a solution with any desired boundary conditions, including the complex ones. Eq. (3.13) can then be reduced to an equation of the same size with real coefficients,

$$\frac{d}{dR}\begin{bmatrix}\underline{\underline{a}}\\[12pt]\underline{\underline{b}}\end{bmatrix}=\begin{bmatrix}\underline{\underline{\dot{B}PA}}-\underline{\underline{B P \dot{A}}} & \underline{\underline{\dot{B}PB}}-\underline{\underline{B P \dot{B}}}\\[12pt]\underline{\underline{\dot{A}PA}}-\underline{\underline{A P \dot{A}}} & \underline{\underline{\dot{A}PB}}-\underline{\underline{A P \dot{B}}}\end{bmatrix}\begin{bmatrix}\underline{\underline{a}}\\[12pt]\underline{\underline{b}}\end{bmatrix}\qquad(3.14)$$

where

$$\underline{\underline{U}}^{\pm}=(1/2)^{1/2}(\underline{\underline{B}}\pm i\underline{\underline{A}})\qquad\alpha^{\pm}=(1/2)^{1/2}(\underline{\underline{b}}\mp i\underline{\underline{a}})\qquad(3.15)$$

and the matrix $\underline{\underline{P}}$ (purely imaginary for a real basis set X) is defined in (2.4). The above equations are convenient for numerical work since their integration requires real arithmetic only.

IV. A NUMERICAL EXAMPLE - TRANSITION PROBABILITIES
AND THE SCATTERING WAVEFUNCTION FOR AN ATOM-ION COLLISION

In this section a numerical solution of the Eq. (3.14) derived
in Sec. II is presented. The transition probabilities and the
scattering wavefunction are evaluated for an atom-ion collision
in the two-state approximation.

The physical system chosen is the excitation collision

$$He^+ + Ne(2p^6) \rightarrow He^+ + Ne^*(2p^53s) \tag{4.1}$$
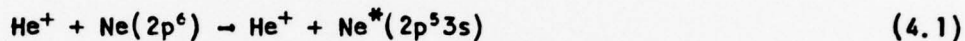
at collision energy of 70.9 e.v. (2.60566 Hartrees). The above inelastic
process has been studied extensively in the past decade, both computational-
ly[15,25-28], and experimentally.[29-31] The main features of the experimental
results can be explained by a two-state curve crossing model in which the
coupling results from the radial part of the Hamiltonian only, so that the
angular momentum is preserved throught the collision. The coupled equations
in the diabatic representation which describe mathematically the process
with the above approximations can be written as[15]

$$\left\{ \begin{bmatrix} p^2 & 0 \\ 0 & p^2 \end{bmatrix} + \begin{bmatrix} V_{11} & V_{12} \\ V_{12} & V_{22} \end{bmatrix} \right\} \begin{bmatrix} \psi_{11} & \psi_{12} \\ \psi_{21} & \psi_{22} \end{bmatrix} = E \begin{bmatrix} \psi_{11} & \psi_{12} \\ \psi_{21} & \psi_{22} \end{bmatrix} \tag{4.2}$$

The potential matrix elements used are those of ref. 15.

Eq. (4.2) can be converted into two coupled equations in the adiabatic representation by solving the algebraic problem of diagonalization of the matrix $\underline{V}$, which for two states can be performed analytically. The transformation matrix is given by (A.7) and the resulting set of adiabatic equations can be written in matrix form as

$$\left\{\begin{bmatrix} p & P_{12} \\ P^*_{12} & p \end{bmatrix}^2 + \begin{bmatrix} W_{11} & 0 \\ 0 & W_{22} \end{bmatrix}\right\} \begin{bmatrix} \psi_{11} & \psi_{12} \\ \psi_{21} & \psi_{22} \end{bmatrix} = E \begin{bmatrix} \psi_{11} & \psi_{12} \\ \psi_{21} & \psi_{21} \end{bmatrix} \tag{4.3}$$

where

$$W_{1,2} = \frac{1}{2}(V_{11} + V_{12}) \pm [(V_{11} - V_{12})^2/4 + V_{12}{}^2]^{1/2} \tag{4.4}$$

and

$$P_{12} = 1(dt/dR)^{1/2}/(1+t^2); \quad t = (V_{22} - V_{11})/2V_{12} \tag{4.5}$$

The method from Sec. 2 can now be applied to (4.3) directly. The corresponding uncoupled adiabatic equations are given by

$$\begin{bmatrix} p^2 & 0 \\ 0 & p^2 \end{bmatrix} + \begin{bmatrix} W_{11} & 0 \\ 0 & W_{22} \end{bmatrix} \begin{bmatrix} \phi_{11} & \phi_{12} \\ \phi_{21} & \phi_{22} \end{bmatrix} = E \begin{bmatrix} \phi_{11} & \phi_{12} \\ \phi_{21} & \phi_{22} \end{bmatrix} \tag{4.6}$$

The solutions of (4.6) which are needed for solving (4.3) were constructed numerically using Gordon's method.[8,32] Any desired solution of (4.6) is then written as

$$
\begin{bmatrix} \psi_{11} & \psi_{12} \\ \psi_{21} & \psi_{22} \end{bmatrix} = \begin{bmatrix} A_1 & 0 \\ 0 & A_2 \end{bmatrix} \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} + \begin{bmatrix} B_1 & 0 \\ 0 & B_2 \end{bmatrix} \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix} \tag{4.7}
$$

where A_i and B_i are two linearly independent real solutions of each
(4.6): A_i is the solution which decays exponentially in the classically
forbidden region and is given by $A \sim (1/2k_i)^{1/2} \cos(k_i r - \xi_i)$ asympotically
in the classically allowed region. B_i is the other linearly independent
solution normalized to a unit Wronskian, which is given asympotically in
the classically allowed region as $B \sim (1/2k_i)^{1/2} \sin(k_i r - \xi_i)$.

The initial conditions on the matrices $\underline{a}$ and $\underline{b}$ used in the calculations are

$$
\underline{\underline{a}} = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}; \qquad \underline{\underline{b}} = \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix} = \begin{bmatrix} 0 & 0 \\ 0 & 0 \end{bmatrix} \tag{4.8}
$$

The integration of the equations was started at a value of the radial coor-
dinate low enough to obtain converging results for the transition probabilities
to three significant figures. Starting the inelastic integration at 0.1 a.u. to
the left of the outermost turning point was usually sufficient. The integra-
tion was stopped at a value of $R = R_f$ where the matrices $\underline{a}$ and $\underline{b}$ became
constant to the same accuracy. (~ 5 a.u.) The matrices $\underline{\underline{\alpha}}^+(R_f)$ and $\underline{\underline{\alpha}}^-(R_f)$ were
then constructed from the final values of the matrices $\underline{a}$ and $\underline{b}$ according
to (3.15) and an inelastic scattering matrix S' was constructed

$$
\underline{\underline{S}}' = \underline{\underline{\alpha}}^+(R_f)\,[\underline{\underline{\alpha}}^-(R_f)]^{-1} \tag{4.9}
$$

The conventional scattering matrix S can be obtained in terms of the matrix
S' by comparing their definitions (2.15) and (4.9). Since the reference
solutions $F_{ii}^{\pm}$ (2.14) and $U_{ii}^{\pm}$ (3.5) differ by the elastic phase shift $\eta_i = \ell_i \pi/2 - \xi_i$
the relation between $\underline{\underline{S}}$ and $\underline{\underline{S}}'$ is given by

$$
\underline{\underline{S}} = \underline{\underline{\eta}}\,\underline{\underline{S}}'\,\underline{\underline{\eta}} \tag{4.10}
$$

where $\underline{\underline{\eta}}$ is a diagonal matrix with elements

$$\underline{\underline{\eta}}_{ii} = \exp\left(i\eta_i\right) \qquad\qquad (4.11)$$

— The numerical integration was performed by solving (3.14) using a standard coupled differential equations integration subroutine.[32] The results of the calculation and several angular momenta for total energy of the collision of 70.9 e.v. (2.60566 A.U.) are given in the second column of table 1. The third column numbers are from Ref. 28 and have been obtained by solving the equivalent set of equations in the diabatic representation (4.2)

The elements of the first row of the matrices $\underline{\underline{a}}$ and $\underline{\underline{b}}$ as a function of R for the actual imposed initial condition in the numerical integration, (Eq. (4.8)) are presented graphically on part b of Figure 1. Those are the quantities calculated as a function of R in the actual numerical integration and the virtual absence of any oscillations or instabilities is evident from the figure.

The first row of the wavefunction on the l.h.s. of (4.6) as a function of R in the vicinity of the "crossing point" is presented graphically on part c of the Figure. The highly oscillating wave functions shown here are the quantities which would have to be followed numerically by the integration routine if a solution of (4.3) had been attempted directly for the same initial condition.

The physically meaningful boundary condition on the matrices $\underline{\alpha}^+$ and $\underline{\alpha}^-$ at large R is that the matrix $\underline{\alpha}^-(R_f)$ be a unit matrix. In that case, the first and second rows of the matrices $\underline{\alpha}^+$ and $\underline{\alpha}^-$ for every R correspond to the solution for which the particle is incoming in the lower or upper channel, respectively. The matrices $\underline{\alpha}^+$ and $\underline{\alpha}^-$ corresponding to such boundary conditions which will be denoted with $\underline{c}^+$ and $\underline{c}^-$ can be obtained by post-multiplying the matrices $\underline{\alpha}^+$ and $\underline{\alpha}^-$ for every R with the inverse of the final value of the matrix $\underline{\alpha}^-$ namely $[\underline{\alpha}^-(R_f)]^{-1}$.

$$\underline{c}^{\pm}(R) = \underline{\alpha}^{\pm}(R)[\underline{\alpha}^-(R_f)]^{-1} \tag{4.12}$$

The elements of the first row of the wavefunction $\underline{\psi}$ corresponding to such boundary condition can be obtained at every R by pre-multiplying the matrices $\underline{c}^+$ and $\underline{c}^-$ with the reference solution matrices $\underline{U}^+$ and $\underline{U}^-$ as defined by (3.5), respectively, and are shown on part d of the figure.

V. DISCUSSION

The method for treating inelastic collisions presented here is based
on an explicit separation of the elastic and inelastic effects of the col-
lision. It is shown that the oscillatory structure of the coupled equations,
which is one of the main sources of difficulties·in developing a solution
method, is almost entirely due to elastic effects. The solutions of the
elastic part of the problem, which can be obtained relatively easily, can
then be used to derive a set of equations for the purely inelastic effects.
The variables in the latter are a measure of the probability of finding the
particles in a given internal state at any point in the collision and the
virtual absence of oscillations in their change with the interparticle dis-
tance in the model problem treated here is evident from the numerical cal-
culations presented.

The present formalism can be shown to be the exact analog of some
semiclassical[34] and uniform semiclassical[27] treatments in the literature.
To obtain the latter one only needs to substitute the semiclassical or
uniform semiclassical approximation to the elastic wavefunction: the equa-
tions for the inelastic effects remain the same. In such a way the present
formalism offers a simple way of deriving the above approximations and
also allows one to express the final equations in simple
form.

Introducing some additional classical limit approximations, as shown
in ref. 34, reduces the present equations to the classical path equations,
which forms a convenient framework for intuitive interpretation of the variables
in the inelastic equations in terms of their classical limit behavior. A
more detailed discussion of the semiclassical aspects of the problem is
given elsewhere.[5,35]

APPENDIX.

1. Transformations between the equations in different representations

The coupled equations (2.8, 2.9), rewritten here

$$(\underline{I}p + \underline{P})^2\underline{\psi} + \underline{V}\underline{\psi} = E\underline{\psi} \tag{A.1}$$

can be converted into the adiabatic representation using the unitary transformation $\underline{M}$ which diagonalizes the potential energy matrix $\underline{V}$

$$\underline{MVM} = \underline{V}^a \tag{A.2}$$

to transform the solution matrix $\underline{\psi}$

$$\underline{\psi}^a = \underline{\tilde{M}}\underline{\psi} \tag{A.3}$$

The tilde symbol ~ above denotes a hermition conjugate matrix.

The transformed equations in the adiabatic representation are obtained by substituting (A.2) and (A.3) in (A.1) and premultiplying the resulting equation by $\underline{\tilde{M}}$, yielding

$$(\underline{I}p + \underline{P}^a)\underline{\psi}^a + \underline{V}^a\underline{\psi}^a = E\underline{\psi}^a \tag{A.4}$$

where

$$\underline{P}^a = \underline{\tilde{M}}(\underline{I}p + \underline{P})\underline{M} \tag{A.5}$$

Similarly, the coupled equations (A.1) can be converted into the diabatic representation by means of the unitary transformation which diagonalizes the kinetic energy part of the Hamiltonian

$$\underline{N}(\underline{I}p + \underline{P})^2\underline{\tilde{N}} = Ip^2 \tag{A.6}$$

A solution of the second order differential equation (A.6) is given by the solution of the first order differential equation

$$p\underline{\tilde{N}} = \underline{P}\underline{\tilde{N}} \tag{A.7}$$

Eq. (A.7) gives a rigorous definition of the diabatic representation for the case of atomic collision problems where it cannot be easily defined in terms of the asymptotic basis sets.[3] However, since the transformation or a set of equations in the adiabatic representation into the diabatic representation requires solving a coupled set of differential equations (A.7), it is practically never used.

The definition of the adiabatic and the diabatic representation given in Sec. 2 is based on the choice of the internal-orientational basis set that leads to a particular representation. Alternatively, the adiabatic representation has been defined[3] by the vanishing of the off-diagonal elements of the matrix $\underline{\underline{V}}$, and the diabatic one by the vanishing of the diagonal elements of $\underline{\underline{P}}$ in (2.9). When the basis set X is complete the two alternative definitions are identical.[5,35] When the basis set used to derive the equations is not complete they are however different. The "adiabatic" set of equations obtained by diagonalizing the potential matrix in a finite diabatic set of equations corresponds to using an approximate expansion of the eigenfunctions of the internal part of the hamiltonian at every R in terms of the asymptotic internal states. The "diabatic" set of equations obtained by diagonalizing the kinetic energy matrix operator in a finite adiabatic set of equations similarly corresponds to equations obtained by using an approximation to the asymptotic internal wavefunctions in terms of the local eigenfunctions of the internal hamiltonian at every R, and it is weakly dependent on R.

2. Symmetry Properties of the Coupled Equations

Eq. (2.8) is a self-adjoint second order matrix differential equation in the sense that the hermitian conjugate of the solution is an integrating factor for the equation and can be used to reduce its order by one.[36]

Premultiplying (2.11) by the hermitian conjugate of the solution, taking the

hermitian conjugate of the matrices on both sides, and subtracting one gets

$$\widetilde{\underline{\Psi}} p^2 \underline{\psi} - (p^2 \widetilde{\underline{\Psi}}) \underline{\psi} + 2[\widetilde{\underline{\Psi}} \underline{P} p \underline{\psi} + (p \widetilde{\underline{\Psi}}) \underline{P} \underline{\psi} + \widetilde{\underline{\Psi}} (p \underline{P}) \underline{\psi}] = 0 \qquad (A.8)$$

where the explicit form of $\underline{T}$ (2.9) has been used.

Rearranging, (A.8) can be written as

$$p[\widetilde{\underline{\Psi}} p \underline{\psi} - (p \widetilde{\underline{\Psi}}) \underline{\psi} + 2(\widetilde{\underline{\Psi}} \underline{P} \underline{\psi})] = \quad p \underline{F}(\widetilde{\underline{\Psi}}, \underline{\psi}) = 0 \qquad (A.9)$$

or integrating both sides, after substituting $p = -i(d/dR)$

$$\widetilde{\underline{\Psi}} \, p \, \underline{\psi} - (p \widetilde{\underline{\Psi}}) \underline{\psi} + 2(\widetilde{\underline{\Psi}} \underline{P} \underline{\psi}) = \underline{F}(\widetilde{\underline{\Psi}}, \underline{\psi}) = \text{const} \qquad (A.10)$$

Hence, the hermitian conjugate of the solution of (2.11) is an integrating

factor for the same equation and the equation is self-adjoint.   Equation

(A.10) can be viewed as the analog of the flux conservation relation for

the Schrodinger equation.   It can be obtained from the flux conservation

relation for the Schrodinger equation simply by substituting the basis

set expansion for the wavefunction and integrating over the $\underline{r}, \underline{\Omega}$ dependence.[5]

The value of the constant matrix $\underline{F}$ can be evaluated at R=0 where the wave-

function matrix $\underline{\psi}$ vanishes and it is zero.

The self-adjoint property of the coupled equations or their "Hermicity"

has been a point of some confusion in the literature.   It was argued (c.f.

ref. 3, sec. 9) that the matrix $\underline{B}$ (2.7) is not hermitian and therefore

the coupled equations are not Hermitian.   While the matrix $\underline{B}$ does indeed

represent a non self-adjoint term in (2.9) the matrix operator $\underline{P}p$ is also

not self adjoint. The easiest way to recognize this point is to notice that $\underline{P}p$

is a product of two noncommuting self adjoint matrix operators so that the

whole Hamiltonian matrix operator is self-adjoint, as one would expect.

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Table I: The Transition Probabilities $|S_{12}|^2$ for He + Ne $\rightarrow$ He + Ne* at collision energy of 70.9 ev and different angular momenta

Angular Momentum	$|S_{12}|^2$ (this work)	$|S_{12}|^2$ (ref. 28)
200	0.215	0.215
300	0.146	0.146
310	0.202	0.202
320	0.0941	0.0941
330	0.0226	0.0226

Legend to Figure 1

The adiabatic potential energy matrix elements W_{ii} and the coupling matrix element P_{12} are shown in (a) as a function of the radial coordinate R. The W_{11}, W_{22} and E are in Hartrees, while $P_{12}/10$ is in $bohr^{-1}$. The first row elements of the matrices $\underline{\underline{a}}$, solid line, and $\underline{\underline{b}}$, dashed line, obtained by solving numerically (3.14) with the initial conditions (4.6) are shown in (b). The wavefunction (4.5) for the same initial conditions is shown in (c). The actual wavefunction, corresponding to no incoming wave in the upper channel is shown in (d), where the solid line describes the real part and the dotted line the imaginary part of the wavefunction. In each case (b) to (d), the upper curve or curves refer to channel 2 (the more highly internally excited channel), and the lower curve or curves refer to channel 1. The structure of the adiabatic potential matrix elements around the avoided crossing is shown in the insert on part a.

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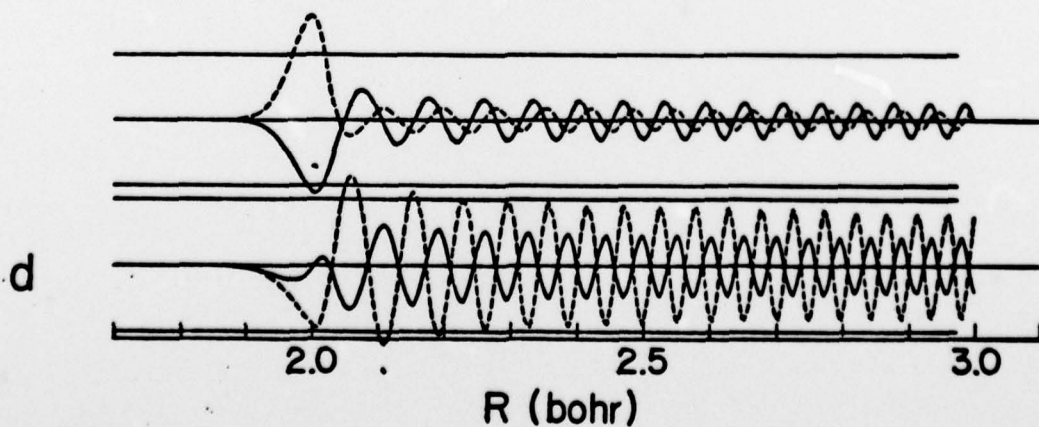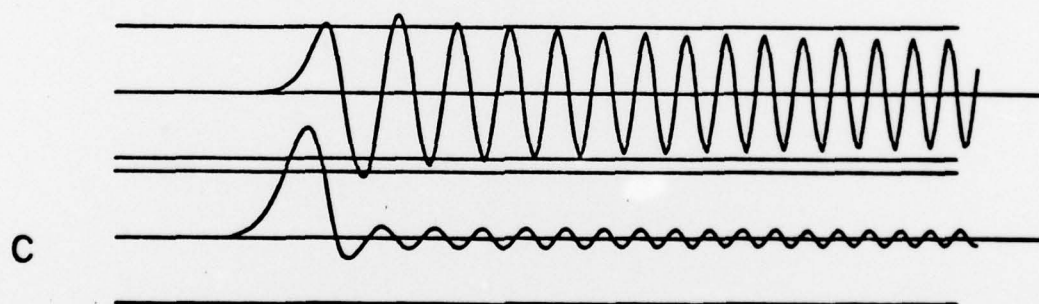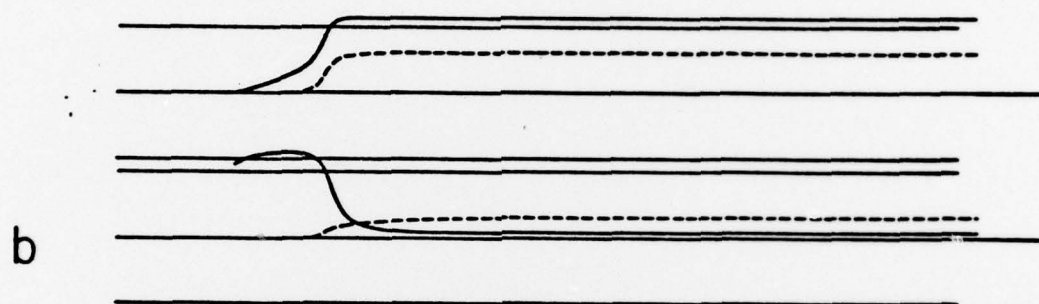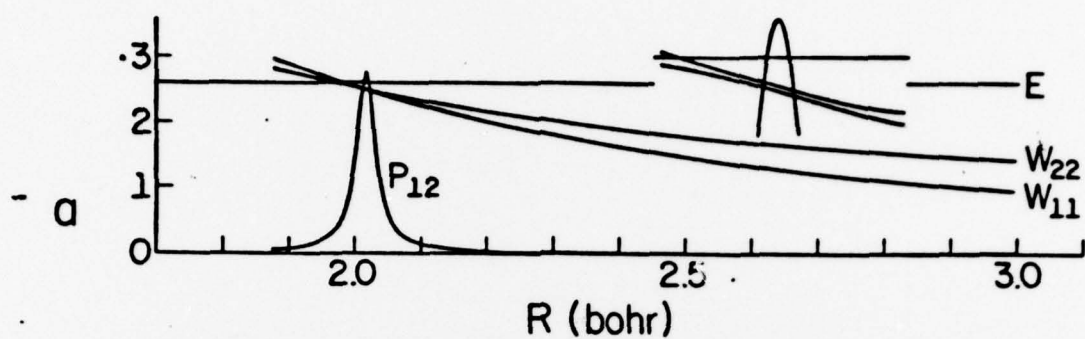
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